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FUEL CELLS (PART II). PREOXIDATION OF THE

SINTERED NICKEL ELECTRODE

by T. Takahashi and K. Ito

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FUEL CELLS (PART II)

PREOXIDATION OF THE SINTERED NICKEL ELECTRODE[*]

by

Takehiko Takahashi[**] and Kaname Ito[**]

1. Introduction

Porous carbon and sintered nickel electrodes are widely used in $O_2 - H_2$ fuel cells. The Ni electrodes are preferable to the carbon electrodes since the nickel ones are mechanically stronger and more resistant to high temperatures. Nickel electrodes can be used at 200—300°C, and in the presence of gases under high pressure. As a result, the current output per unit area of electrode surface is greater. For example, a Bacon cell equipped with double Ni electrodes generates 600 ma/cm^2 at 0.8 v (240°C) when the pressures of the O_2 and H_2 are 54 atm.[1,2] This cell is one of the best of those known.

In the Bacon cell, when sintered Ni is used as the material for the oxygen electrode, it is oxidized, forming green, electrically resistant NiO; as a result, it cannot be used for more than about ten hours. Various attempts have been made to prevent the oxidation. Potassium silicate and aluminate have been added, with some desirable results, but these compounds tended to retard the reaction at the electrode, and thus cannot be used in practice.[2]

The best method is to form an oxide film on the surface of the electrode by oxidation in air at elevated temperatures. Since the oxide film must be highly conductive, Bacon treated Ni electrodes with oxygen in the presence of Li^+ and successfully prepared high-conductivity nickel oxide films (entectic compound of lithium oxide and nickel oxide, hereafter referred to as Ni(Li) oxide). He used the above electrode for the oxygen electrode.

In order to obtain more detailed information about the formation of Ni(Li) oxide films, we carried out the oxidation of Ni plates and studied the formation of the films and the behavior of Li^+. We also investigated the effects of lithium on the electrical conductivity and the polarization characteristics of the electrodes.

2. Experimental

2.1. Materials

The nickel plates used were 0.5 × 1 × 10 cm in size and the surface was oxidized as described below. Prior to the oxidation, the Ni plate was dipped in

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hot, concentrated hydrochloric acid for three minutes to make the surface chemically uniform.

2.2. Formation of Ni(Li) oxide films

### 2.2.1. Experimental conditions for the formation of films

Commercial reagent grade LiOH was employed as the source of Li^+. The entectic compound of NiO and Li_2O is usually prepared from NiO and Li_2CO_3.[3] However, the solubility of Li_2CO_3 in water is low (1.33 g/100 g water at 20°C), and thus it is difficult to prepare aqueous solutions of Li^+ over a broad range of concentrations. We used 1, 5, and 10% aqueous solutions of LiOH. Nickel plates were dipped in the LiOH solution, dried at 120°C and subsequently oxidized by heating in air at 600, 700 and 800°C for 1 hour. After oxidation, the sample plates were cooled rapidly, and residual LiOH was removed by washing with 2N acetic acid solution and repeatedly with distilled water. LiOH and Li_2CO_3 (formed from atmospheric CO_2) were removed by the treatment with dilute acetic acid, but Ni(Li) oxide is insoluble in dilute acetic acid.[5] Therefore, only the lithium ions that were incorporated into the film remained.

2.2.2. Determination of Li^+

Lithium in the films was determined by flame photometry.[5] Li_2CO_3, purified by reprecipitation[6], was used as the standard. A working standard solution (2000 ppm Li^+) was prepared. Although it has been reported[5] that Ni^{++} does not interfere greatly in the determination of Li^+, we set up a calibration curve for the determination of Li^+ in the range from 0 to 20 ppm in the presence of divalent nickel ions (we first determined the required time of dissolving the nickel plates which would yield an Ni^{2+} concentration of 500 ppm). Based on this calibration, the determination of Li^+ was as follows. In order to avoid possible contamination and interference from Na^+ and Kt, polyethylene bottles and beakers were used throughout, except for such operations as evaporating to dryness, in which case quartz beakers were used. A preoxidized nickel plate (10 × 1 cm) was washed free of unreacted Li^+ as above, was dipped into 10 ml of concentrated, reagent grade hydrochloric acid, and boiled for 3 − 6 minutes to dissolve the oxide film. The plate was removed when the film had dissolved completely and the solution was evaporated to dryness to drive off the excess HCl. After cooling, a small amount of water was added to the residue and the resulting solution was transferred to a graduated cylinder and diluted to 100 or 50 ml. This solution was used for determination of the intensity of the Li^+ spectrum by means of a flame photometer.

2.2.3. Amounts of Ni(Li) oxide films formed

When NiO and Li_2CO_3 are mechanically mixed and strongly heated (800° − 1200°C), Li^+ enters the crystal structure of NiO, replacing some Ni ions and forming entectic compound (Li−O−Ni−O−). A number of divalent nickel ions equal to the number of lithium ions thus incorporated must become trivalent in order to maintain electrical neutrality. Therefore, the decomposition of the entectic can be expressed as[9]

$$Li_x Ni^{2+}_{(1-2x)} Ni^{3+}_{(x)} O \qquad (1)$$
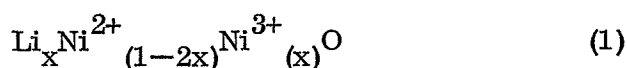
The entectic compounds prepared, starting with metallic nickel, should also have the same chemical composition.

The weight increase of a nickel plate and the weight of Li^+ in the oxide film are designated as a_g and b_g, respectively. The weight of oxide film formed can thus be expressed by the equation

$$M = \left(\frac{O+Ni}{O}\right)a - \left[\frac{(Li+O)Ni}{Li \times O}\right]b \qquad (2)$$
$$= 4.66a - 1.21b$$

From Eq. 2, the weights (mg) of film formed under various conditions were calculated from the experimental values of a_g and b_g. Fig. 1 shows the relation between the Li^+ concentration = the solution and the weight of film formed per unit area. In Fig. 2, the amount of film is plotted against preoxidation temperature. The amount of oxide film was found to be moderately dependent on the preoxidation temperature when the Li^+ concentration in the solution was up to 5%: it increased as the preoxidation temperature was raised from 600 to 800°C. The
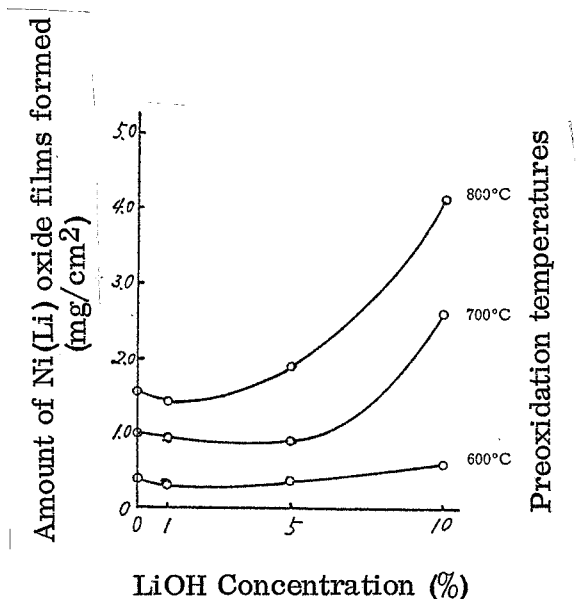

Fig. 1. Amounts of Ni(Li) oxide film formed on a Ni plate

amount formed was about the same as that in the absence of LiOH. However, the amount increased considerably with temperature at the higher Li^+ concentration (10%); it rose as high as 2.6 and 4.1 mg/cm^2 at 700 and 800°C, respectively. In these cases, the Ni(Li) oxide film did not adhere well and the surface became rough. These last experimental conditions are therefore not suitable for producing electrodes, since their mechanical strength would be low.
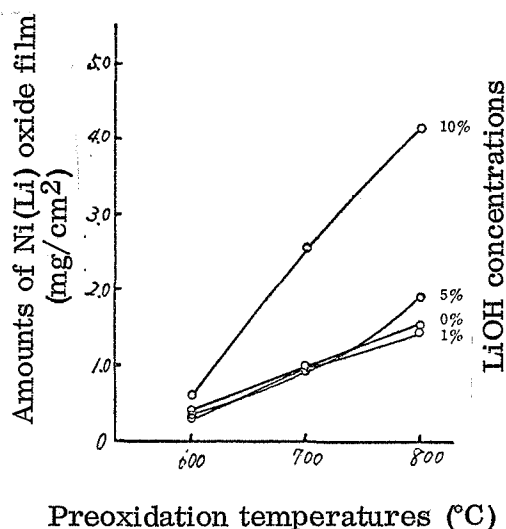
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Fig. 2. Amounts of Ni(Li) oxide film formed on a Ni plate

2.2.4. Amount of Li^+ in the Ni(Li) oxide films

A greenish film (NiO) was formed when a Ni plate was heated at 600 — 800°C in air but in the absence of Li^+, while a black oxide film was formed when it was heated to the same temperatures in the presence of Li^+. This was, as mentioned earlier, the entectic compound of Li_2O and NiO. The quantity of Li^+ in the Ni(Li) oxide film determined its properties. Therefore, we considered it important to determine it.

Fig. 3 gives the results of the determination of the amount of Li^+ in an oxide film per unit area; Fig. 4 shows the same figures as percentages. It is clearly seen that the Li^+ content increased. It can be concluded, however, that
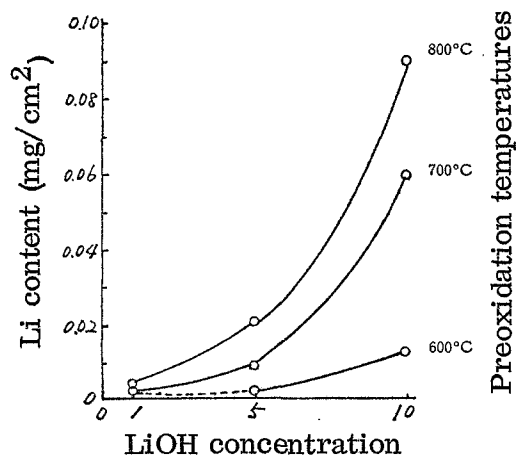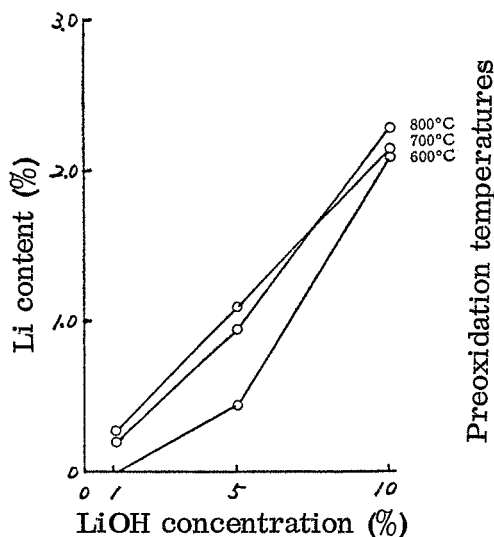

Fig. 3. Contents of Li in Ni(Li) oxide films

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Fig. 4. Contents of Li in Ni(Li) oxide films

the effect of temperature was much greater than that of Li^+ concentration, since we had already established that the rate of formation of the film itself was greater at higher temperatures.

2.3. Resistance of Ni(Li) oxide films

2.3.1. Method of measurement

The electric resistance of the Ni(Li) oxide films formed on a Ni plate varies from point to point. The fluctuation is particularly great for the thin oxide film formed at 600°C. Thus, it is not possible to obtain a precise value of the specific resistance. Since the resistance also varies depending on the oxidation conditions, the resistance of the films was determined at room temperature as follows. An aluminum foil electrode (0.5 × 0.5 cm) cemented to a polyethylene rod was placed in contact with the sample, and a pressure of 2 kg/cm² was applied. The electrical resistance between the foil and the plate was measured. The average of several measurements at different sites is shown in Fig. 5.

2.3.2. Results of the resistance determinations

The specific resistance of a pure Ni oxide film formed on Ni oxide when it is further oxidized in an oxidizing atmosphere at 1200°C is very high, about 10^8 ohm-cm. However, the resistance decreases greatly when the Ni oxide is heated in the presence of Li_2CO_3. According to Verway et al.[7] the specific resistance is 100, 12 and 17 ohm-cm at Li^+ concentrations of 0.2, 1, and 2%, respectively. As is seen in Fig. 5, the resistance of an oxide film formed in the absence of Li^+ is very high ($10^5 \sim 10^7$ ohms). However, the resistance decreased sharply when even a very small amount of Li^+ was incorporated; for example, it was reduced to 100 — 300 ohms when the Li^+ concentration was 0 — 0.25%, the value obtained when the plate was treated with 1% LiOH solution prior to oxidation. The resistance was found to be practically independent of the oxidation temperature as long as the Li^+ concentration was kept within the range
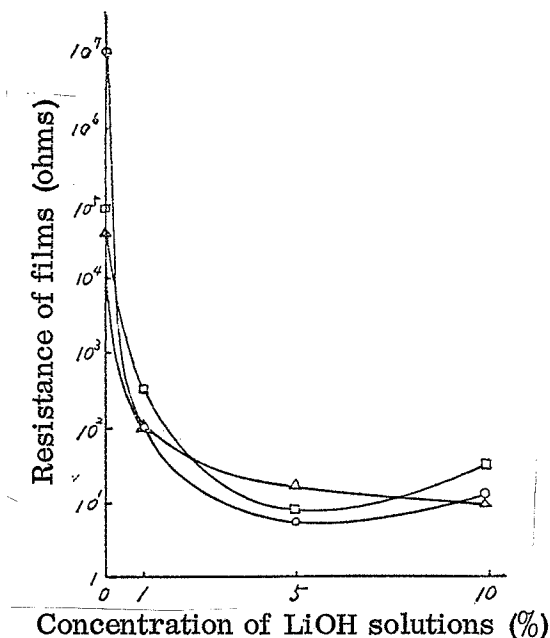
Fig. 5. Resistance of Ni(Li) oxide films found on Ni plates

Preoxidation temperatures: ○ 800°C, □ 700°C, △ 600°C. Measurements
were made at room temperature. For other conditions,
see text.

used in the present work. As is seen from Fig. 4, the Li^+ concentration in the
oxide film was proportional to its concentration in the solution. Therefore, it
can be said that the resistance values shown in Fig. 5 are determined by the Li^+
concentration in the Ni(Li) oxide films. The manner in which the resistance is
controlled by the Li^+ concentration is somewhat similar to that shown by Verway
et al.[7] We concluded that electrodes with low-resistance oxide films could be
produced if the Li^+ concentration was held within the range of 5 — 10%.

2.4. Polarization characteristics

2.4.1. Measurement of polarization

In order to determine the effect of the oxidation conditions on the
polarization characteristics (operating as an oxygen electrode), we measured the
polarization of electrodes (1 × 0.05 × 5 cm) prepared under the conditions described
above. The experimental conditions were normal pressure and 200°C. It was
very difficult to determine the characteristics using a Bacon cell, since the
pressure had to be high. A concentrated KOH solution (KOH = H_2O = 30 = 10) was
used as the electrolyte. The apparatus is illustrated in Fig. 6. A silver plate
was used as the electrode (O_2/Ag electrode). All the results given here are
relative to the potential of this electrode [0 v] [*].

*) We chose this electrode as our reference because its absolute potential was
found in preliminary experiments to be highly reproducible, and very little
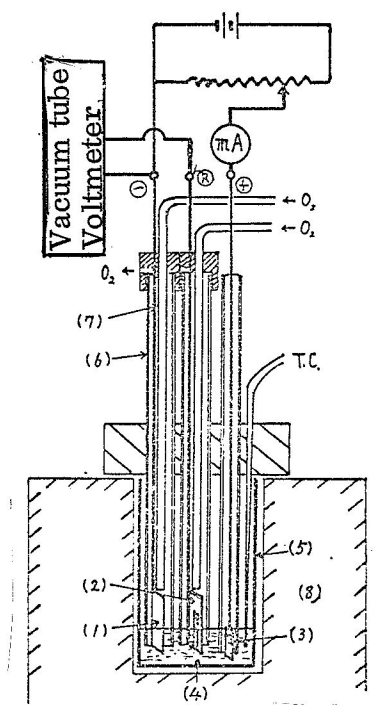polarization was observed.

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Fig. 6. Apparatus for the measurement of the polarization characteristics.
(1) tested electrode; (2) supplementary electrode (O_2/Ag electrode);
(3) electrode (Pt electrode); (4) electrolyte solution (KOH = H_2O = 30 = 10);
(5) Ag crucible; (6) Al tube; (7) Cu tube; (8) electric furnace

In order to ensure that the electrode was operating as an oxygen electrode, we determined the relation between the potential and time (Fig. 7) at a current of 0.2 m/electrode, while permitting O_2 or N_2 to flow. With oxygen, the polarization was in the range of 2—50 mv and was independent of time. When N_2 was passed, however, the polarization was from 400 to 1000 mv and did depend on time. These results clearly indicated that the electrode was operating as an oxygen electrode when O_2 was passed and that in the presence of N_2 it was operating as a Ni(Li) oxide electrode. In the figure, the untreated Ni plate gave a very low voltage, —0.8 v, at which it appeared to be operating as a gas electrode. The voltage became —1.0 v immediately after the reaction started; this value corresponds to the potential of hydrogen generation.

Fig. 8 shows the polarization characteristics of a Ni plate operating as an oxygen electrode. A Ni plate gave —0.8 v against an O_2 (Ag) electrode when it was used as an oxygen electrode. This low value of potential may be attributed to a loss of energy through adsorption of O_2 on the electrode. This will be investigated in more detail in future studies. Fig. 8 shows the polarization characteristics of a Ni(Li) oxide electrode operating as an oxygen electrode. It is seen that no potential drop due to adsorption of O_2 took place and the electrode operated satisfactorily.
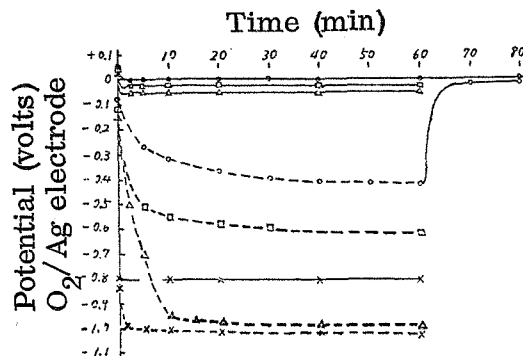
Time (min)

Fig. 7. Change of polarization (as an O$_2$ electrode) of preoxidized
Ni electrodes with time

Preoxidation temperatures   o   800°C ⎤   x   no treatment

                              □   700°C ⎬   —— operated in O$_2$

                              △   600°C ⎦   ———— operated in N$_2$

Size of plate electrodes: 5 ×1 cm; electrolyte solution: KOH = H$_2$O = 30 = 10;
current = 0. 2 mg/electrode; working temperature 200°C; LiOH concentration
in the pretreatment solution, 10%

Current density (ma/electrode)

—— 10% ⎤ Concentration   ○ 800°C ⎤
····· 5% ⎥ of LiOH solu-   □ 700°C ⎬ Preoxidation temperatures
—·— 1% ⎬ tions   △ 600°C ⎦
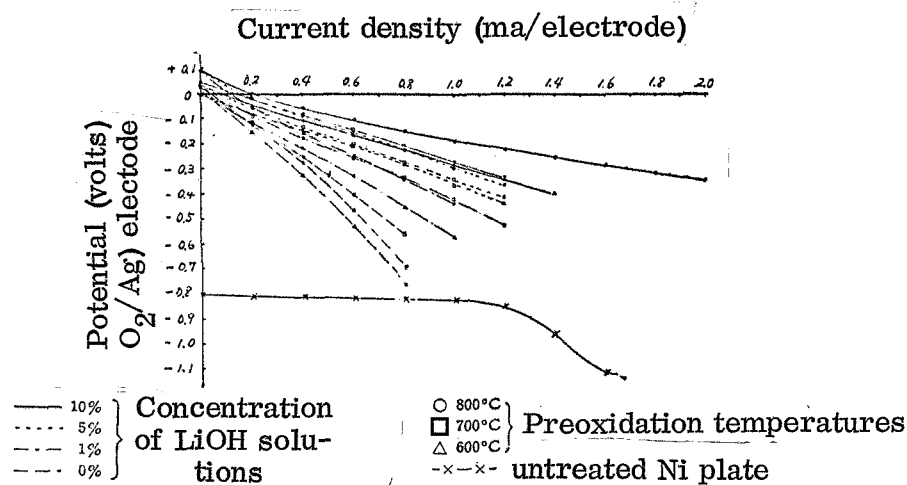——· 0% ⎦   -x—x- untreated Ni plate

Fig. 8. Polarization characteristics (as an O$_2$ electrode) of preoxidized
Ni plate electrodes. Oxygen flow rate = 130~150
ml/min; size of electrodes working condition were
the same as in Fig. 7

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The conditions of oxide film formation affected the polarization characteristics. The polarization was considerable with electrodes that had been oxidized in the absence of Li^+; it was much smaller for electrodes oxidized in the presence of Li^+ and were thus conductive. The higher the Li^+ content in the oxide films and the higher the temperature, the lower was the polarization. In general, three different types of polarization can be considered in an electrochemical reaction; concentration polarization, activation polarization and resistance polarization. Of these, concentration polarization was considered to be negligible under our experimental conditions, that is, at high temperature and with a highly concentrated KOH solution as the electrolyte. The structure of the electrodes and the small currents were also factors supporting the above assumption. Even if the concentration polarization were of some significance, it would be identical, under identical experimental conditions and identical currents. Therefore, the polarization observable in Fig. 8 must be attributed to activation and resistance polarization. The fraction of the resistance polarization due to the resistance of the electrolyte (IR drop) may be considered negligible, since the resistance of the solution (R) and the current (I) were both very small. However, the resistance of the oxide film may not be neglected. As Fig. 5 shows, the resistance of the untreated oxide film was about 10^6 times that of an electrode oxidized in the presence of excess Li^+. This resistance decreases with increase in temperature because the material is a semiconductor, i.e., the resistance at high temperature would be even lower if the negative temperature coefficient[7] were taken into account, but it is still not negligible. Thus, it is reasonable to assume that the resistance of the oxide film is the major factor in the polarization. The higher the conductivity (that is, the higher the Li^+ concentration in the film) the smaller the polarization. It was experimentally shown that the polarization increased when the oxidation temperature was higher. At higher temperatures, the rate of oxide film formation was greater, leading to thicker films. The physical properties of the film surface varied. The decrease in the polarization might be due to activation at the surface. In order to obtain decisive answers to the above problems, more detailed future work will be required.

3. Discussion

3.1. Effect of K^+ and Na^+ on the formation of Ni oxide films

The basic requirement for the preparation of very conductive semiconductors from highly resistant crystals such as NiO is that the two semiconductor components must be of different chemical valence and that one of the two must be capable of being incorporated within the crystal lattice of the other without disturbance.

There are two possibilities for preparing such semiconductors. One involves the use of a crystal lattice with defects, at which sites the valence of the element is changed; the other is the employment of a crystal lattice in which other elements may be incorporated[7]. The latter is the so-called controlled valence semiconductor we used in our work. One requirement for an element which can be incorporated within the crystal lattice of another element is that its atomic or ionic radius must be close to that of the other material. The atomic radius of Ni^+ is 0.78 A*; therefore, an ion with an ionic radius close to

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* Reported by Goldschmidt.

this value is needed. The ionic radius of Li^+ is exactly 0.78 A.* The second ionization potential of Li is 73.5 ev, which is greater than the third ionization potential of Ni: 35 ev[7]). Therefore it follows that a high-conductivity semiconductor with small lattice defects can be made if a nickel plate is oxidized in the presence of Li^+, as was the case in the present work.
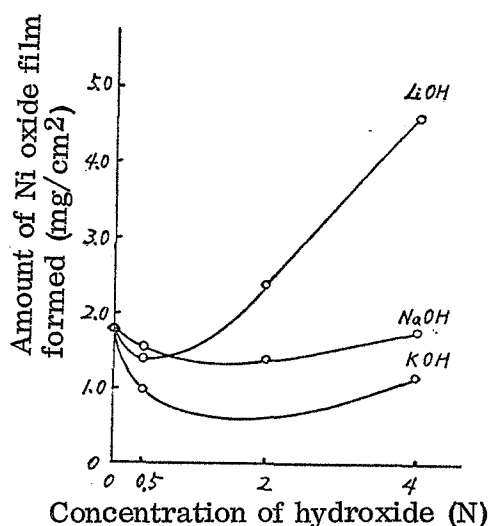
Preoxidation temperature 800°C

Fig. 9. Effects of Na^+ and K^+ on the formation of Ni oxide films

One might consider it possible to obtain electrically conductive Ni oxide films from NaOH, KOH and others instead of LiOH. However, it is not likely because the radii of Na^+ and K^+ ions are 0.98 and 1.33 A*, respectively, and these values are considerably larger than that of the Ni^{++} ion; hence, the conductivity would decrease according to the theory of atomic valence control explained above. To confirm this, NaOH and KOH solutions of the same concentration as the LiOH solution were prepared, and Ni plates were treated with them in the same manner and oxidized at 800°C. The results are shown in Figs. 9 and 10). As can be clearly seen, the resistance of the oxide films was great even though the amounts formed were small. The resistance was 10^5 ohms for NaOH and 10^6 ohms for KOH. This indicates that the theory of atomic valence control assumed

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* Reported by Goldschmidt.
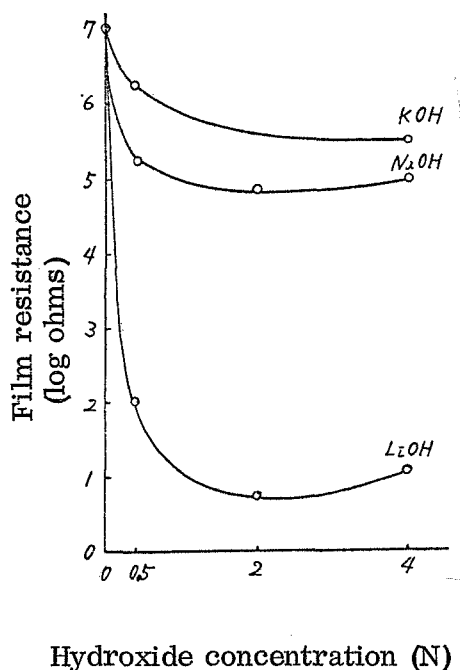
Hydroxide concentration (N)

Fig. 10. Resistance of Ni oxide films treated with NaOH or with KOH before oxidation. Measurements at room temperature. For other conditions, see Fig. 5.

for the preparation of Ni(Li) oxide films was correct.

3.2. Conditions for oxidation of Ni electrodes

Bacon et al.[2] carried out corrosion tests on Ni plates which had been oxidized in a KOH solution containing dissolved O_2 at 200—300°C and under 50—60 atm pressure. The Ni plates were very resistant to corrosion: a plate with a 2 mg/cm^2 Ni(Li) oxide film could be used for more than 10,000 hours at 300°C.

Below we give the optimal conditions for the oxidation of Ni electrode, deduced from the above information and our experimental results:

1. The concentration of the LiOH solution in which the Ni plates are immersed should be in the range from 5 to 10%.

2. The Ni plates should be heated for one hour in the air at 700—800°C or 650—700°C after immersion in 5% and 10% LiOH soludion, respectively. That is, heating at 600°C does not afford Ni(Li) oxide films which are satisfactorily corrosion resistant and a Ni(Li) oxide film formed by heating at 800°C after immersion in 10% LiOH solution tends to become too thick and fragile. On the other hand, the Li content in the oxide film becomes too low, so that the conductivity of the film also becomes too low, when the Ni plate is treated with a

LiOH solution of a concentration below 5%.

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